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ON THE ALKYL SULPHATES.

By F. W. BUSHONG, Kansas City University.

Read before the Academy, at Topeka, January 1, 1903.

TWO lowest members of the series of neutral alkyl sulphates, dimethyl sulphate and diethyl sulphate, have long been known. In 1870 Chapman¹ obtained impure diisoamyl sulphate by passing sulphur dioxide into isoamyl nitrite. Stempnewsky² states that alkyl sulphates are formed by the interaction of silver sulphate with alkyl haloids, but Nef³ found that while this method yields normal dipropyl sulphate and diisoamyl sulphate it does not furnish diisopropyl sulphate nor diisobutyl sulphate, and accounts for this by pointing out that these esters possess very low dissociation points. On this account, he suggests that the only possible method which presents itself for their synthesis at low temperature is the interaction of sulphuryl chloride or its esters with alcoholates.

Following this suggestion, I have prepared ethyl isopropyl sulphate, ethyl isobutyl sulphate and ethyl isoamyl sulphate from chlorsulphonic ethyl ester and sodium alcoholates, and diisopropyl, diisobutyl and diisoamyl sulphates from sulphuryl chloride and the sodium alcoholates.

The reaction between sulphuryl chloride and sodium alcoholates is complicated and the yield of alkyl sulphate cut down by the dissociation of the sulphuryl chloride into sulphur dioxide and chlorine. I wish, on this account, to investigate this reaction further before stating my results, and at present describe only my experiments with chlorsulphonic ethyl ester.

CHLORSULPHONIC ETHYL ESTER, ITS PREPARATION AND PROPERTIES.

Soon after the constitution of sulphuric acid and its relation to chlorsulphonic acid and to sulphuryl chloride had been established, R. Williamson⁴ prepared chlorsulphonic ethyl ester "by direct combination of chloride of ethyl with anhydrous sulphuric acid. Its composition was determined by finding the weight of the product obtained by combining a known weight of SO_3 with chloride of ethyl."

Purgold⁵ found that in this reaction at least two of the three possible isomers are formed, and his work has, in part, been confirmed by Armstrong.⁶ He also proved that the ester thus obtained is identical with the chloranhydride of ethyl sulphuric acid, which he made by

1. Ber. d. chem. Ges. 3, 920 (1870).

3. Liebig's Annalen 318, 40 (1901).

2. Ber. d. chem. Ges. 11, 514 (1878).

4. Jr. Chem. Soc. 10, 100 (1857).

5. Liebig's Annalen 149, 124 (1869), Ber. d. chem. Ges. 6, 502 (1873).

the action of phosphorus pentachloride upon dry potassium ethyl sulphate, as well as with a body prepared by Wilm⁶ by the action of fuming sulphuric acid upon chlorcarbonic ethyl ester, carbon dioxide being liberated.

M. Müller⁷ obtained the same compound, together with isethionic acid, by passing ethylene into chlorsulphonic acid.

It was also obtained by Sandmeyer⁸ by the addition of ethyl hypochlorite to sulphur dioxide.

On passing chlorine gas, free from air, into a solution of sodium bisulphite in ten per cent. aqueous alcohol, I have found that chlorsulphonic ethyl ester is at first formed rapidly, but is destroyed as soon as a considerable quantity of hydrochloric acid has been formed.

Through Claesson's method⁹ free ethyl sulphuric acid is now easily accessible, and from this Nef¹⁰ has prepared chlorsulphonic ester by means of phosphorus pentachloride, but I have had difficulty in removing the last traces of phosphorus from the ester thus made.

The chlorsulphonic ethyl ester used in the experiments hereafter described was made from sulphuryl chloride and alcohol by the following modification of Behrend's method:¹¹

Sulphuryl chloride (Kahlbaum's) was put into a distilling flask fitted with a doubly perforated stopper, through which were inserted the stem of a dropping funnel and a glass tube connected with a calcium chloride drying tube. The end of the glass tube was drawn out until almost capillary, and dipped below the surface of the sulphuryl chloride. The delivery stem of the distilling flask led to a wash-bottle containing water and provided with a safety tube. The wash-bottle was connected with an aspirator, and air was drawn through the liquid for the double purpose of keeping the liquid constantly stirred and of carrying away the extremely irritating fumes. The flask was immersed in a freezing mixture. Absolute alcohol (a little in excess of one molecule) was admitted drop by drop from the dropping funnel. When all the alcohol was admitted the freezing mixture was removed, but the air current was maintained about half an hour longer, until the liquid acquired the temperature of the room and became perfectly colorless. After standing, two layers may be distinguished; the lighter and smaller consists mainly of ethyl sulphuric acid, and the heavier of nearly pure chlorsulphonic ester. The lower layer, after washing with cold water, drying with calcium chloride, and distilling under reduced pressure, yields over sixty per cent. of the theoretical quantity of the pure ester.

I. 0.3372 gram substance gave 0.5528 gram BaSO₄.

6. *Jr. prak. Chem.* (2) 1, 244 (1870).

7. *Ber. d. chem. Ges.* 6, 227 (1873).

8. *Ber. d. chem. Ges.* 19, 860 (1886).

9. *Jr. prak. Chem.* (2) 19, 231 (1879).

10. *Liebig's Annalen* 318, 40 (1901).

11. *Jr. prak. Chem.* (2) 15, 28 (1877).

II. 0.4108 gram substance required 28.20 cc. AgNO_3 solution, representing 0.0984 gram Cl.

III. 0.3450 gram substance required 23.53 cc. AgNO_3 solution, representing 0.0821 gram Cl.

	Calculated for $\text{Cl-SO}_2\text{-OC}_2\text{H}_5$.	I.	Found. II.	III.
S	22.18	22.51
Cl	24.52	23.96	23.80

Chlorsulphonic ethyl ester is a colorless, limpid liquid, possessing a sharp, pungent odor, irritating to the eyes and exciting tears. Its boiling-point under a pressure of 14 mm. is 52° , and under 20 mm. 58° . The specific gravity is 1.3630 at 18° . It is soluble in ligroin, chloroform, and ether, but attacks ether when warmed. It is also soluble in fuming nitric acid, and is precipitated unchanged by the addition of water. Water affects it only slightly in the cold, even after standing with it for weeks; but on heating, decomposition quickly sets in. Thus, 4.8 grams of the ester heated in a distilling flask containing 40 cc. water, gave 150 cc. of ethyl chloride, or 16 per cent. of the theoretical amount. The decomposition of the ester by alcohol has been shown by Claesson to yield ethyl chloride, hydrogen chloride, ethyl sulphuric acid, ether, and a small amount of diethyl sulphate.

ACTION OF CHLORSULPHONIC ETHYL ESTER UPON SODIUM ALCOHOLATES.

1. Upon Sodium Ethylate. Twenty-five grams (2 mols.) freshly prepared sodium ethylate, dried at 180° in a hydrogen stream under reduced pressure, were suspended in 100 grams purified gasoline (b. p. 110° – 125°). Twenty-five grams chlorsulphonic ethyl ester were slowly added by means of a dropping funnel, the mixture being continually agitated and kept cool in an ice-salt freezing mixture. After the ester had all been added, the temperature was allowed to rise to about 10° , and was kept there until the odor of the ester was no longer noticeable. The gasoline solution was then decanted, filtered, and subjected to distillation from a water-bath, and yielded ethyl ether, which after rectification weighed 2.85 grams. The residue of salts was washed with absolute ether and the washings were added to the gasoline from which the ether formed in the reaction had been removed as above described. On then removing the ether and gasoline by distillation at reduced pressure, 9.92 grams diethyl sulphate, distilling between 96° at 18 mm. and 96° at 14 mm., were obtained—a yield of 32.2 per cent. After being washed with ether, the salts were dissolved in water and the solution was saturated with carbon dioxide, then evaporated to dryness under reduced pressure. By digestion with absolute alcohol, 12.2 grams sodium ethyl sulphate were obtained

(47.6 per cent.) The residue, insoluble in alcohol, gave, on dissolving in water—acidifying with hydrogen chloride, etc.—2.05 grams of barium sulphate, which corresponds to 1.25 grams (5 per cent.) sodium sulphate.

2. Upon Sodium Isoamylate. ETHYL ISOAMYL SULPHATE, $C_2H_5O-SO_2-OC_5H_{11}$. Twenty-two grams ($1\frac{1}{2}$ mols.) sodium isoamylate, dried at 220° in a stream of hydrogen under reduced pressure, were suspended in 100 cc. absolute ether, and cooled in a freezing mixture of ice and salt, and 19.5 grams chlorsulphonic ethyl ester added; drop by drop. The temperature was allowed to rise slowly to about 15° and it was observed that the sodium isoamylate gradually dissolved, and that salt did not separate even after half an hour's standing at room temperature. On heating the mixture, however, under a reversed condenser, much salt was deposited. The ethereal filtrate was first distilled at about 100 to 150 mm. pressure in order to remove the excess of ether, the amyl alcohol, and amyl ethyl ether. The two last substances were formed in considerable amounts but were not quantitatively separated. The residual oil was distilled at about 18 mm. pressure; there was much charring with evolution of sulphur dioxide, but the distillate, after washing with dilute sodic hydrate and drying with calcium chloride, yielded 5 grams (37 per cent.) of pure ethyl isoamyl sulphate (described below). The salt residue insoluble in ether was worked up in the same manner as the salts formed from sodium ethylate, already described. The absolute alcoholic extract weighed 7.4 grams and proved to be sodium isoamyl sulphate, although possibly sodium ethyl sulphate may have been present in small quantity. Considered as sodium isoamyl sulphate, the amount found was 29 per cent. of the theory. The remaining salt residue yielded 6.88 grams $BaSO_4$, corresponding to 4.19 grams (21.8 per cent.) of sodium sulphate.

In a second experiment, 34 grams sodium isoamylate, 150 cc. ether and 30 grams chlorsulphonic ethyl ester were used. The ethereal solution was not heated under the reversed condenser, as in the preceding experiment, but on adding about 25 cc. of cold water a thick gelatinous mass of salts was precipitated, which dissolved on adding (125 cc.) more water. The ethereal solution was washed frequently with water, dried with calcium chloride, and subjected to fractional distillation under reduced pressure. The oil that remained after the removal of the amyl alcohol and amyl ethyl ether was, however, not directly distilled, but first again taken up in ether, washed with dilute caustic alkali, dried with calcium chloride, and then distilled at reduced pressure. Thus 20 grams (49 per cent.) of pure ethyl isoamyl sulphate were obtained.

0.4636 gram substance gave 0.5646 gram BaSO_4 (Carius).

Calculated for		Found.
$\text{C}_2\text{H}_5\text{O}-\text{SO}_2-\text{OC}_5\text{H}_{11}$.		
S	16.34	16.72

Ethyl isoamyl sulphate is a colorless oil, resembling diethyl sulphate, but its odor is less agreeable, although somewhat like that of bananas. Its boiling-point was found to be $127-128^\circ$ at 15 mm.; specific gravity, 1.079 at 20° (Westphal); index of refraction for sodium light, 1.4118 (Abbe). It is insoluble in and is not affected by cold water, but dissolves readily in alcohol, ether, and ligroin. Heated above 140° , rapid decomposition begins.

3. Upon Sodium Isobutylate. ETHYL ISOBUTYL SULPHATE, $\text{C}_2\text{H}_5\text{O}-\text{SO}_2-\text{OC}_4\text{H}_9$. Proceeding exactly as in the experiment last described, 25 grams (1.5 mols.) sodium isobutylate, freshly prepared and dried at $180-190^\circ$ in a stream of hydrogen under reduced pressure, were suspended in about 100 cc. absolute ether, and treated with 30 grams chloresulphonic ethyl ester. On adding water to the clear ethereal solution obtained, a copious gelatinous precipitate was instantly formed. The products isolated were:

Ethyl isobutyl sulphate, 18.7 grams, or 50 per cent.

Sodium isobutyl sulphate, 9.6 grams, or 26 per cent.

Sodium sulphate, 3.2 grams, or 11 per cent.

The ethyl isobutyl sulphate obtained boils at 108° under a pressure of 13 mm. and possesses the specific gravity 1.098 at 23° (Westphal). Its index of refraction for sodium light is 1.4068 (Abbe). It is a colorless oil, insoluble in water, having an odor similar to that of mandrake. In a sulphur determination (Carius),

0.6276 gram substance gave 0.8183 gram BaSO_4 .

Calculated for		Found.
$\text{C}_2\text{H}_5\text{O}-\text{SO}_2-\text{OC}_4\text{H}_9$.		
S	17.60	17.90

4. Upon Sodium Isopropylate. ETHYL ISOPROPYL SULPHATE, $\text{C}_2\text{H}_5\text{O}-\text{SO}_2-\text{OC}_3\text{H}_7$. On treating 27 grams (2 mols.) sodium isopropylate, suspended in about 100 cc. absolute ether, with 22.8 grams of chloresulphonic ethyl ester, the following products were obtained:

Ethyl isopropyl sulphate (crude oil), 16.2 grams, 62.2 per cent.

Sodium isopropyl sulphate, 7.5 grams, 29.3 per cent.

Sodium sulphate (not weighed).

Ethyl isopropyl sulphate is less stable than the other alkyl sulphates here described, and consequently there is much loss in distilling it even at reduced pressure. Its boiling point is 105° at 18 mm. pressure; the specific gravity, 1.143 at 21° (Westphal), and the index of refraction for sodium light, 1.4062 (Abbe). For the analysis a

distilled portion was taken up in ether, washed with dilute caustic soda, and dried with calcium chloride. The ether was then removed by heating to 60° in a vacuum.

0.4904 gram substance gave 0.6664 gram BaSO₄.

Calculated for		Found.
C ₂ H ₅ O-SO ₂ -OC ₃ H ₇ .		
S	18.95	18.65

The sodium isopropyl sulphate obtained closely resembles sodium isobutyl sulphate in appearance, soapy feel, and solubility in water and alcohol. A portion of it was hydrolyzed by means of hydrochloric acid and the alcohol thus obtained boiled between 79.5° and 82°. This on oxidation gave acetone, as was proved by converting it into indigo by condensation with o-nitro benzaldehyde.

I wish to gratefully acknowledge that the results I have to present were made possible by my appointment, three years ago, to a fellowship in the University of Chicago. My work was, however, seriously interfered with by sickness, and is not yet completed.